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(71) Applicant: **AUSIMONT S.p.A.**
31 Foro Buonaparte
I-20121 Milano(IT)

(72) Inventor: **Cavallotti, Claudio**
Via Lorenteggio 3
I-20146 Milano(IT)
Inventor: **Troglia, Claudio**
Via R. Sanzio 27
I-20149 Milano(IT)
Inventor: **Garaffa, Roberto**
Via San Domenico 75 (al Corso Europa)
I-80127 Napoli(IT)

(74) Representative: **Zanoli, Enrico et al**
Spherilene S.r.l., Tecnologie e Proprietà Industriale, Via Principe Eugenio, 1/5
I-20155 Milano (IT)

(54) Process for purifying phthalimidoperoxycaproic acid (PAP) which removes chlorinated solvent impurities from it.

(57) Process for purifying phthalimido-peroxycaproic acid (PAP) from chlorinated solvents, by dissolving it in a polar and volatile solvent selected from alcohols, ketones and aliphatic esters, and a following crystallization thereof and solvent stripping.

Preferred solvents are aliphatic esters, in particular ethyl acetate.

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The present invention relates to a process for purifying phthalimido-peroxycaproic acid (PAP) from the impurity constituted by the chlorinated solvents used in the synthesis and entrapped inside PAP crystal lattice.

More in particular, the present invention relates to a process for purifying PAP in which the chlorinated solvents, which constitute the impurity, are removed by means of a solvent showing particular characteristics.

The process for preparing PAP is known from European Patent Application No. 490,409.

According to this process, phthalimido-caproic acid (PAC) is converted into peroxy acid, by means of H_2O_2, in the presence of a strong acid, in a double phase system, in the presence of an organic solvent constituted by a halogenated aliphatic hydrocarbon selected from dichloromethane and trichloromethane. The resulting PAP is recovered from the organic phase by low-temperature crystallization, or solvent removal under vacuum (stripping).

By means of analyses of the end product (PAP) (gaschromatography, X-ray fluorescence), the presence of the chlorinated solvents used for the synthesis, was determined. PAP crystals contain such entrapped solvents in an amount comprised within the range of from 500 to 2,500 ppm.

It is known that the halogenated aliphatic compounds are toxic and potentially carcinogenic; they may consequently create pollution problems. Therefore, the content of chlorinated solvents entrapped inside PAP should advisably be reduced down to an extremely low level in all products designed for consumers' usage. Such a reduction or removal is recommended in the case of industrial use of PAP as a bleaching agent in medium-low temperature detergent compositions.

The purpose of the present invention is hence of providing a process which can be performed at an industrial level, in order to eliminate the impurities constituted by the chlorinated solvents entrapped inside the crystal lattice of PAP, obtained according to the process as disclosed in European Patent Application No. 490,409.

The present Applicant found now that the use of a solvent, used after the synthesis of PAP and showing particular characteristics, makes it possible the chlorinated solvents present inside PAP's crystal lattice, also at an industrial level.

Therefore, the subject-matter of the present invention is a process for purifying phthalimido-peroxycaproic acid (PAP) from chlorinated solvents, by dissolving said PAP and subsequent crystallization and evaporation of the solvents (stripping), characterized in that said PAP is dissolved in a polar and volatile solvent, selected from the group consisting of alcohols, ketones and aliphatic esters.

More in particular, an object of the present invention is a process for purifying PAP from chlorinated solvents by means of a dissolution thereof and subsequent crystallization or evaporation of solvents (stripping), characterized in that said PAP is dissolved in a solvent belonging to the class of aliphatic esters.

The choice of the solvent used for PAP purification according to the present process is critical.

The solvents suitable for the purposes of the present invention must meet the following requisites:

- they should be good solvents for PAP and for the chlorinated solvent used in the synthesis and entrapped inside the crystals of the obtained PAP;
- they should display good volatility, in order to facilitate the removal of the solvent from the peracid, which volatility however should be not excessively high, in order to jeopardize a possible industrial use teherof;
- they should be not toxic, in order to prevent that a further toxic solvent is entrapped inside PAP crystal;
- they should be completely inert towards the peracid, and display an extremely good oxidation resistance, because the residual traces of solvent used (from 100 to 800 ppm) remaining inside the end product, or of its oxidation products, could, besides creating safety problems, remain inside the peracid crystals, reducing the stability thereof (for example, esters, when into contact with oxygen, form peroxides).

The used solvents, which meet the above mentioned requisites, required by the process according to the present invention, are polar and volatile solvents. In particular, these solvents are aliphatic esters, such as methylacetate and ethylacetate. Preferred solvent is ethylacetate.

The ratio, by weight, of the peracid and the solvent used in order to dissolve it according to the process of the present invention is determined by the solubility of the peracid in the solvent, and preferably is comprised within the range of from 1:2 to 1:8. When aliphatic esters are used as solvents, this ratio is preferably comprised within the range of from 1:3 to 1:6.

The temperature at which the subject process is carried out, is lower than 40 °C, in order to prevent peracid decomposition.

In the process according to the present invention, the crystallization or the solvents evaporation (stripping) may take place both in the precence and in the absence of demineralized water. The peracid is separated in crystal form.

The PAP obtained according to the process of the present invention contains less than 3 ppm of chlorinated solvents. PAP deprived of the chlorinated solvents is stable, in particular when as the solvent in the process according to the present invention, aliphatic esters are used.

According to a preferred embodiment, PAP containing the impurity constituted by a chlorinated solvent is dissolved in a solvent belonging to the class of aliphatic esters, and the purification is carried out by using methodologies known in the art, at a temperature lower than +40 °C.

In order to better understand the present invention and to practice it, some illustrative, non-limitative examples are reported in the following.

EXAMPLES 1 - 4

50 g of PAP was dissolved in each of the solvents reported in following Table 1, at a temperature lower than +40 °C.

So dissolved PAP was treated by means of well-known methodologies [(a) and (b)] in order to recover PAP practically free from chlorinated solvents.

(a) According to the crystallization methodology, dissolved PAP was recrystallized at the temperature of 0 °C. The resulting crystals were filtered off from the suspension, and were subsequently dried in a desicator ($CaCl_2$) for 24 hours at the temperature of +25 °C, under vacuum.

(b) According to the stripping methodology, dissolved PAP was fed, either continuously or batchwise, to a reactor, or to the kettle of a rotary evaporator, at a temperature lower than +40 °C. PAP solution was kept at this temperature under such a residual pressure as to cause the evaporation of the solvent. The peracid was subsequently filtered off, was dried inside a desiccator ($CaCl_2$) under vacuum for 24/48 hours at room temperature.

The operations carried out with the above disclosed [(a) and (b)] methodologies were carried out both in the presence (Examples 2 and 4) and in the absence of demineralized water (Examples 1 and 3).

The process conditions and the results obtained are reported in Table 1.

Table 1

Example No.	Solution fed to purification: Used solvent: Type	Used solvent: Amount, g	PAP to be purified: Purity %	PAP to be purified: Chloroaethanes, ppm	Operating conditions: Dissolution temperature °C	Operating conditions: Stripping temperature °C	Operating conditions: Residual pressure mmHg	Obtained PAP, as dry matter: Amount, g	Obtained PAP, as dry matter: Purity %	Obtained PAP, as dry matter: Chloroaethanes, ppm	Obtained PAP, as dry matter: Residual solvent ppm
1	Methyl acetate	280	99.1	1,200	30°C	--	--	37.5	99.7	<1	690
2	Methyl acetate (H_2O)	260	99.1	1,200	30°C	35°C	100	49	99.2	3	750
3	Ethyl acetate	280	98.7	1,350	35°C	--	--	35.5	99.3	<1	800
3	Ethyl acetate	280	98.9	2,300	35°C	37°C	20	49	98.9	<1	400
4	Ethyl acetate + 4% (H_2O)	263	98.5	1,730	25°C	--	--	35.5	99.3	2	650
4	Ethyl acetate (H_2O)	263	98.5	1,730	25°C	35°C	60	48.5	98.6	<1	480

EXAMPLES 5 - 6

The operating modalities of Examples 1-4 were repeated, however using, as the solvent in PAP purification, an alcohol (ethanol) and a ketone (acetone).

Stripping and crystallization were carried out in the absence of H_2O.
The operating conditions and the results obtained are reported in Table 2.

Table 2

Example No.	Solution fed to purification: Used solvent: Type	Used solvent: Amount, g	PAP to be purified: Purity %	PAP to be purified: Chloroeth-anes, ppm	Operating conditions: Dissolution temperature °C	Operating conditions: Stripping temperature °C	Operating conditions: Residual pressure mmHg	Obtained PAP, as dry matter: Amount, g	Obtained PAP, as dry matter: Purity %	Obtained PAP, as dry matter: Chloroeth-anes, ppm	Obtained PAP, as dry matter: Residual solvent ppm
5	Ethanol	150	98.8	1,900	35°C	--	--	38	99.5	<1	630
5	Ethanol	200	98.5	1,730	35°C	37°C	20	49	98.4	<1	590
6	Acetone	188	98.5	950	30°C	--	--	30	99.2	2	650
6	Acetone	188	98.5	950	30°C	37°C	20	49.5	98.5	<1	370

Stability of purified PAP

The thermal stability of purified PAP was determined by DSC (differential scanning calorimetry) according to ASTM method No. E-537-84 using a PERKIN-ELMER DSC-2C instrument, as well as the loss of peroxide content (%) of said purified peroxid acid.

In order to determine this loss, the tests (A) and (B) were carried out.

According to test (A), 10 g of purified PAP were stored inside a tightly ceiled container, for 30 days at +25 °C.

According to test (B), 0.3 g of purified PAP were stored as a suspension in an inert hydrocarbon (diisopropylbenzene) for 1 hour at +70 °C. The results obtained by examining PAP purified according to Examples 1-6 are reported in following Table 3.

Table 3

Purified PAP				Stability			
		Residual solvent		D.S.C.		Loss of peroxide content (%)	
Example No.	Residual chloromethanes, ppm	Type	ppm	Incipient melting point, °C	Incipient decomposition, °C	Test (A)	Test (B)
1	<1	methyl acetate	690	----	89.5	3.5	7.4
2	3	methyl acetate (H_2O)	750	65	90.5	3.2	7.3
3	<1	ethyl acetate	800	68.3	93.8	0	4.7
3	<1	ethyl acetate	400	73.1	94.8	0	4.5
4	2	ethyl acetate + H_2O 4%	650	71.8	94.2	0	4.6
4	<1	ethyl acetate (H_2O)	480	68.3	94	0	4.6
5	<1	ethanol	680	64.9	85.4	47	12.9
5	<1	ethanol	590	64.5	86.1	44	12.9
6	2	acetone	630	----	88.3	12	9.3
6	<1	acetone	370	65.1	88.7	10	9.2

The data reported in Table 1, 2 and 3 demonstrate that the process according to the present invention removes the impurity constituted by dichloromethane from PAP. The PAP obtained by using the aliphatic esters as the solvent of the process according to the present invention, is very stable.

EXAMPLE 7 (comparison example)

The hexane used for comparison purposes would be capable of dissolving the chlorohydrocarbon impurity entrapped inside PAP crystals, but does not dissolve said PAP and therefore does not meet the requisites required by the solvent to be used in the process according to the invention.

The operating modalities of Examples 1-4 were repeated using n-hexane as the solvent, and separating PAP by stripping at the temperature of +37 °C. The residual pressure was of 20 mm_{Hg}.

The operating conditions and the results obtained are reported in Table 4.

The data shown in Table 4 demonstrate that dichloromethane was not removed from PAP, therefore the purification did not occur.

Table 4

Example No.	Solution sent to purification				Obtained PAP in dry state			
	Used solvent		PAP to be purified					
	Type	Amount, g	Purity, %	Chloromethane content, ppm	Amount, g	Purity, %	Chloromethane content, ppm	Residual solvent, ppm
7	n-Hexane	400	98.7	1,350	50	98.6	1,290	800